Coherent optical spectroscopy of excitons in halide perovskites

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Halide perovskite semiconductors represent an attractive system for optoelectronic and photonic applications. The current understanding of the energy structure of photoexcited charge carriers and exciton complexes, as well as their interactions, binding energy, and relaxation dynamics, is still incomplete. Conventional time-integrated reflectivity or photoluminescence techniques alone often fail to provide clear conclusions about the energy structure due to the inhomogeneous broadening of optical transitions and the complex dynamics of photoexcited carriers. Here, nonlinear optical techniques based on photon echoes or two-dimensional Fourier spectroscopy offer unique insights into the energy structure of perovskite semiconductors.

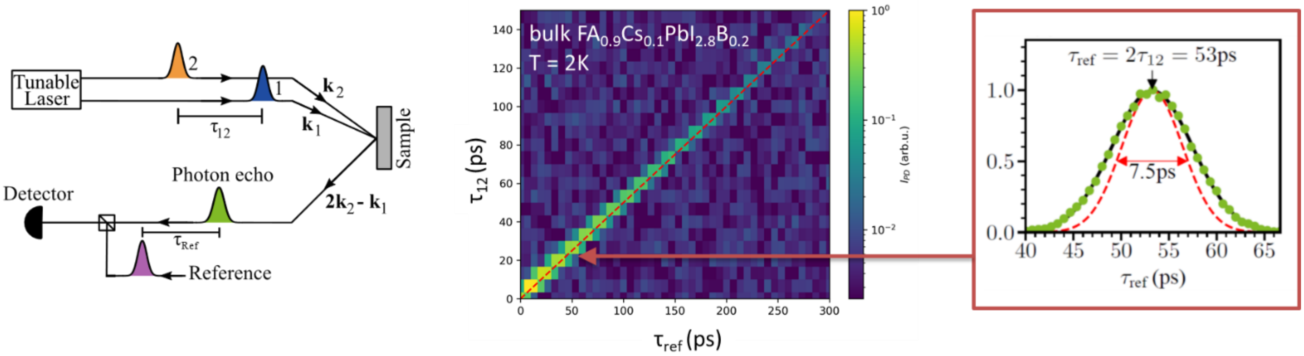

Figure 1: Left: Schematic presentation of two-pulse transient four-wave mixing experiment. Middle: Example of photon echo signal in bulk $(FA,Cs)Pb(I,Br)_3$ single crystal. Right: Cross-section of photon echo signal in time centered at $\tau_{ref} = 2\tau_{12}$.

We investigate the coherent dynamics of excitons in halide perovskite semiconductors of different compositions and dimensionality. Due to the inhomogeneous broadening of optical transitions, coherent optical response is represented by photon echoes even in bulk perovskite crystals (see Fig.1). In mixed $(FA,Cs)Pb(Br,I)_3$ crystals, the magnitude of fluctuations of the energy bandgap is in the order of 10-20 meV. Here, we observe exceptionally long exciton coherence times up to 80 ps at a low temperature of 2 K due to the localization of excitons at the scale of tens to hundreds of nanometers [1]. In this case, the homogenous line of 16 μeV is about three orders of magnitude smaller than the inhomogeneous broadening of optical transitions. This allows us to evaluate fine structure splitting between bright and dark excitons of 300 μeV by analyzing the quantum beats between the exciton spin states in an external magnetic field. Next, the role of exciton-exciton interactions in bulk crystals is evaluated. Here, polarization-resolved transient signals provide rich information about the biexciton binding energy and spin-dependent interactions in dense exciton ensembles [2,3]. Finally, we study coherent optical response from lead-halide nanocrystals where quantum beats in the photon echo signal are observed due to excitons fine structure and interaction with optical phonons.

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References

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